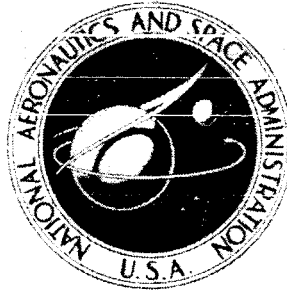


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REACTIVITY OF SIMULATED
LUNAR MATERIAL WITH FLUORINE

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Cleveland, Ohio 44135

1. Report No. NASA TM X-2533		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle REACTIVITY OF SIMULATED LUNAR MATERIAL WITH FLUORINE				5. Report Date April 1972	
				6. Performing Organization Code	
7. Author(s) Patricia M. O'Donnell				8. Performing Organization Report No. E-6741	
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135				10. Work Unit No. 113-34	
				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546				13. Type of Report and Period Covered Technical Memorandum	
				14. Sponsoring Agency Code	
15. Supplementary Notes					
16. Abstract <p>Simulated lunar surface material was reacted with fluorine to determine the feasibility of producing oxygen by this method. The maximum total fluorine pressure used was 53.3 kilonewtons per square meter (400 torr) at temperatures up to 523 K (250° C). Postreaction analysis of both the gas and solid phases indicated that the reaction is feasible but that the efficiency is only about 4 percent of theoretical.</p>					
17. Key Words (Suggested by Author(s)) Oxygen generation Lunar chemistry Fluorination				18. Distribution Statement Unclassified - unlimited	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		22. Price* \$3.00	
				21. No. of Pages 9	

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SUMMARY

Simulated lunar surface material prepared by the Manned Spacecraft Center was exposed to fluorine gas to determine if oxygen could be obtained. The effect of both temperature and pressure on the rate of the reaction were observed. The most stringent conditions studied were a temperature of 523 K (250° C) and a fluorine pressure of 53.3 kilonewtons per square meter (400 torr). Analysis of the residual gas by mass spectrometry indicated that oxygen was liberated. The data suggest that the reaction does not proceed in the same way for the complete duration of reaction time but seems to stifle itself at longer times. The process was not very efficient and only 4 percent of the theoretical amount of oxygen present was liberated.

INTRODUCTION

The successful flights of the Apollos 11, 12, 14, and 15 have made available to the scientific world for the first time several kilograms of lunar material. Analysis of these samples has been underway by investigators throughout the world. The detailed results on the Apollo 11 samples have been reported (refs. 1 and 2), and preliminary results have appeared on the samples from Apollo 12 (ref. 3). Further work on the samples from Apollo 12, 14, and 15 is still in progress. Because of the knowledge gained about the lunar samples, it has been possible to simulate the lunar surface material and thus extend the scope of scientific investigations without depleting the supply of precious material. The present investigation was undertaken on the simulated lunar material to determine the feasibility of oxygen production from lunar surface materials. If man is to function for any long period of time on the moon, the need for a ready oxygen supply becomes immediately apparent. This report presents the results of a preliminary investigation of a proposed method of extracting gaseous oxygen from lunar surface fines by reaction with fluorine.

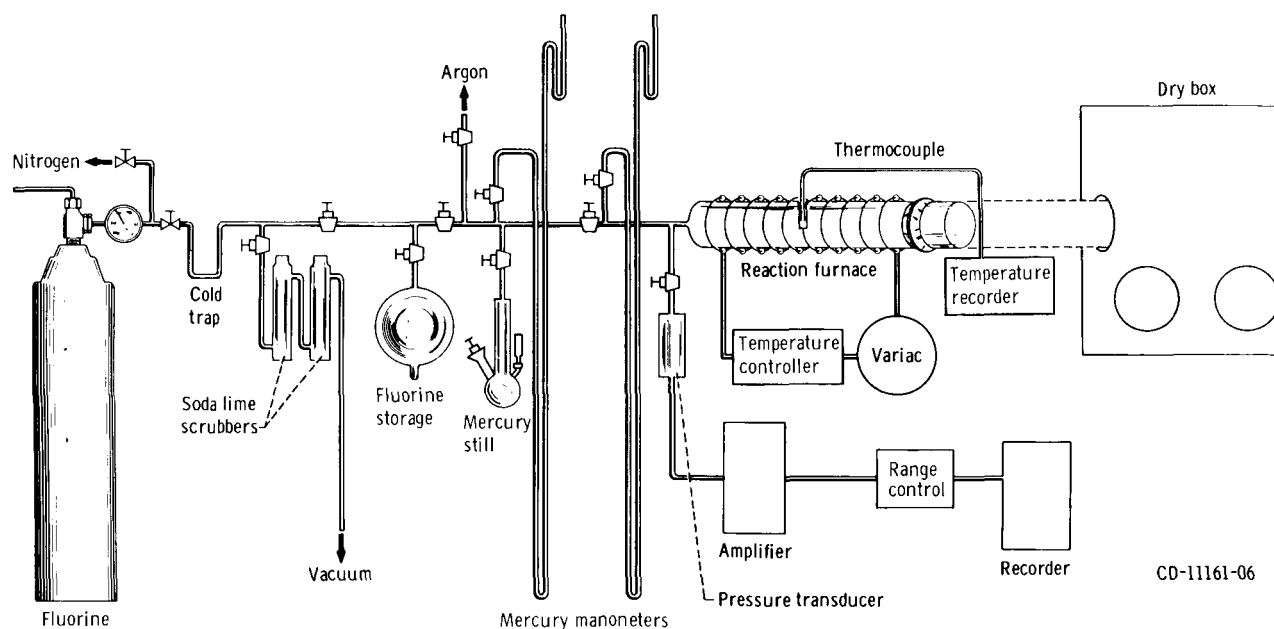
This process, proposed by Dr. W. R. Downs of the NASA-Manned Spacecraft

Center, consists of reacting gaseous fluorine with the material to produce metal fluorides and oxygen. The metal fluorides would then be reacted with potassium vapor to produce potassium fluorides, which would then be electrolyzed using nuclear power to yield fluorine and potassium for recycling. A proposed method for separating the oxygen from the metal fluorides would be to freeze the fluorides out in the lunar shade.

EXPERIMENTAL

Apparatus

The system used to study the oxygen production from simulated lunar materials by reaction with fluorine is shown in figure 1. The vacuum system is Pyrex except for the reaction chamber, which is quartz. Fluorine from the supply tank is passed through a cold trap (157 K (-116° C)) to remove any condensable impurity and stored in the storage bulb. The pressure in the storage and reaction sections are read on the mercury manometers, which have a protective layer of fluorocarbon oil floating on the side that is exposed to the fluorine to prevent any reaction between the fluorine and mercury. Temperature and pressure measuring devices are connected to a recording system as indicated in the figure. The mercury still is used to analyze the residual gas from a run. Excess fluorine is pumped out through two soda lime scrubbers.



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Figure 1. - Apparatus.

Samples

The simulated lunar surface material was prepared by the Lunar Receiving Laboratory at the Manned Spacecraft Center (MSC). The mixture consists of a ground (65 mesh) conglomeration of clinopyroxene, plagioclase, olivine, and ilmenite (all minerals) yielding the following chemical analysis in percent by weight: SiO_2 , 46.1; Al_2O_3 , 13.8; FeO , 13.0; Fe_2O_3 , 1.7; MgO , 7.2; CaO , 10.3; TiO_2 , 5.3; Na_2O , 1.9; K_2O , 0.5; and MnO , 0.2.

The system was passivated by introducing fluorine at increasing temperatures and pressures until further reaction of fluorine with the system was insignificant. For exposure to fluorine the lunar material was contained in alundum boats. The boats had been preconditioned in fluorine at temperatures and pressures well above run conditions and can be considered to be inert. Approximately 0.5 gram of material was used for a run and it was exposed to a total fluorine pressure of 25.6 and 53.3 kilonewtons per square meter (200 and 400 torr). Data were obtained at 298 and 523 K (25° and 250° C). Analysis of the sample after exposure to fluorine was performed at MSC.

RESULTS AND DISCUSSION

By obtaining a pressure-time profile of the gaseous phase during reaction and measuring the amount of oxygen produced from a known quantity of lunar material and fluorine, the chemical reactivity could be assessed.

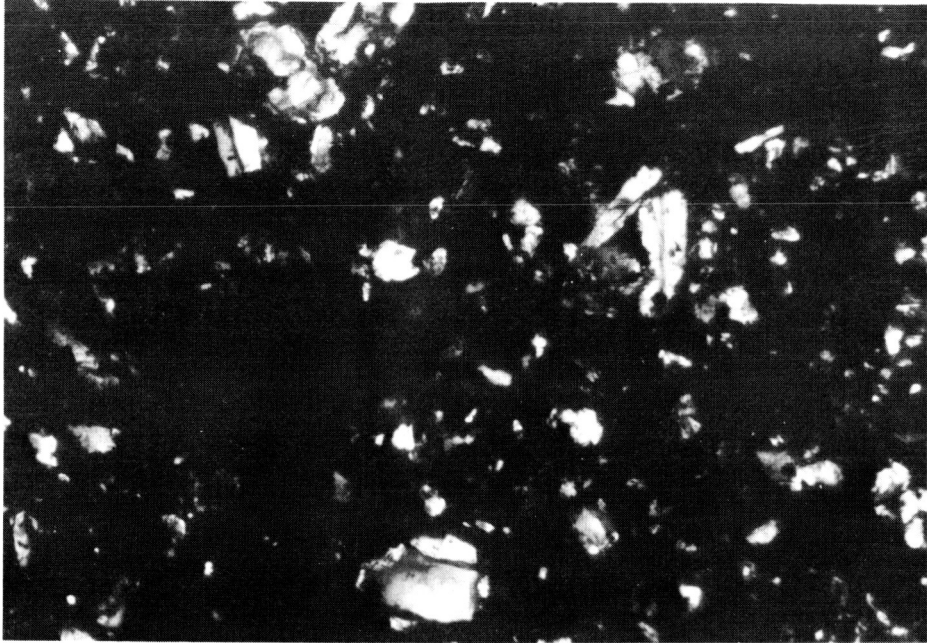
The effect of both temperature and pressure on the weight loss are listed in table I. An increase in weight loss accompanies both an increase in temperature and an increase in pressure.

TABLE I. - WEIGHT LOSS DATA

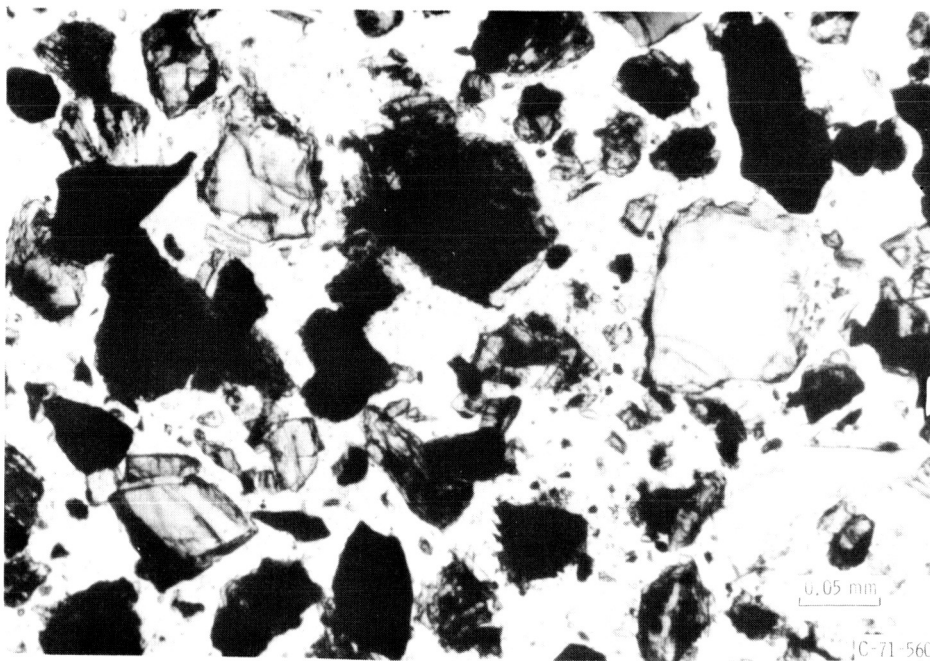
Sample	Sample weight, g	Temperature		Pressure		Weight loss, mg
		K	$^\circ\text{C}$	kN/m^2	torr	
1	0.5637	298	25	26.6	200	1 ± 0.10
2	.5292	523	250	53.3	400	30 ± 0.10
3	.5784	523	250	26.6	200	17 ± 0.10

In the low-temperature run there was no observed temperature rise on exposure of the sample to fluorine. With the higher temperature runs slight temperature fluctuations were observed ($\sim 5^\circ$).

The pressure in the reaction chamber was followed as a function of time. The fluo-



(a) Polarized transmitted light.

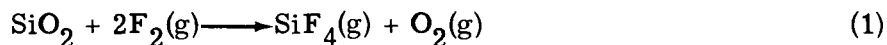


(b) Transmitted light.

Figure 3. - Unreacted lunar soils (simulated).

rine pressure decreases as it reacts but, since some of the products are volatile, the measured pressure corresponds to the sum of the volatile products and the unreacted fluorine. A net pressure decrease is observed, and it is plotted as a function of time in figure 2. Although no quantitative conclusions can be drawn from this plot, if the data are plotted on a log-log plot (right hand plot of fig. 2) a break is observed which indicates that the reaction does not proceed in an identical manner across the complete time span. The reaction could be considered initially close to first order in Δp , the change in the total pressure, following the equation $\Delta p^n = kt$. After approximately 0.5 hour the value of n increases to ~ 3 . The higher the value of n , the more completely does the reaction stifle itself. The accumulation of the products at the reacting interface could be a contributing factor in the decreased reactivity with time.

All samples showed a weight loss. This is not surprising since the major constituent reacts to form a gaseous product at these temperatures according to the following equation



ANALYSIS

Analysis of the samples was done microscopically by Travis J. Allen and D. W. Hutchinson of the Petrology-Minerology Group at the Manned Spacecraft Center's Lunar Receiving Laboratory. The samples were prepared in thin sections and polished. They were observed under both reflected and transmitted light, also loose grains were observed. The samples were (1) the simulated lunar material before reaction and (2) the simulated lunar material that had been reacted with the fluorine gas pressure at 53.3 kilonewtons per square meter (400 torr) and temperature at 523 K (250° C). The loose grain examination showed little if any difference between the two samples. However, the polished thin film sections did show a difference. Both transparent and opaque phases were analyzed. The unreacted material had a sharp, clean appearance, while in the reacted sample changes in color, surface texture, and a loss of sharpness of grain boundaries was observed. No major changes were observed in the large grains of ilmenite, olivine, or plagioclase. The pyroxene phase exhibited the major change. Pyroxene is a mineral class containing simple chains of $(\text{SiO}_3)_n$ mainly with Ca, Mg, and Fe as the positive atoms. The grains of the pyroxene were highly fractured and these made up the bulk of the smaller size fractions. The reacted sample had a pyroxene phase of reddish-yellow brown color. This was not positively identified but could possibly be attributed to the reaction of the iron and magnesium of the pyroxene phase which would form colored fluorides. The unreacted sample by visual observation looks like a grey

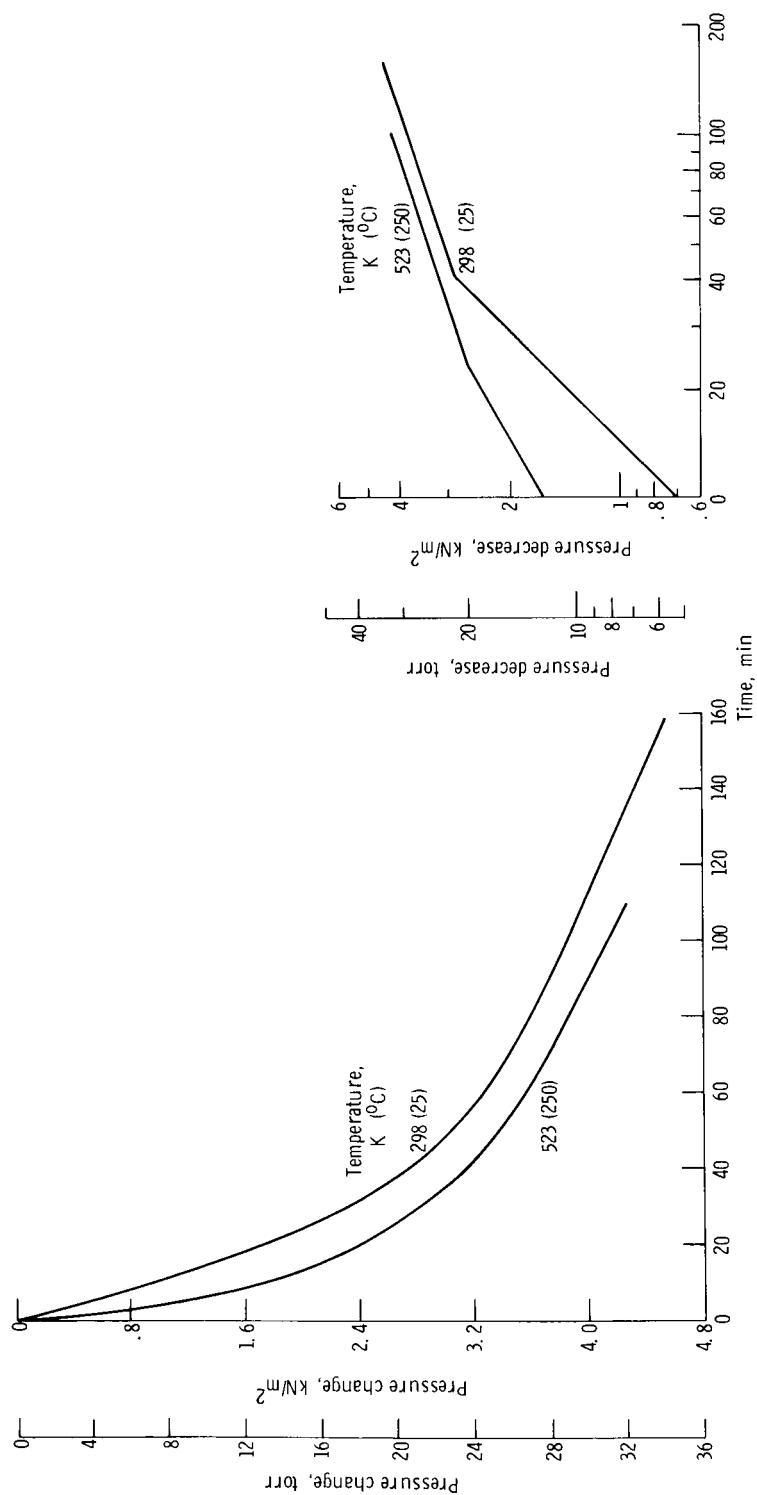
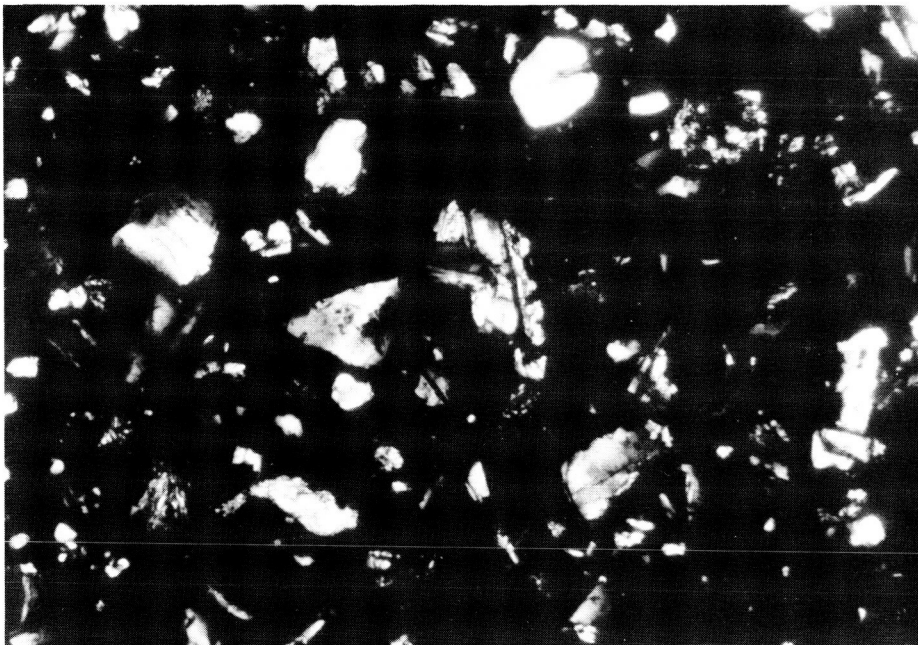
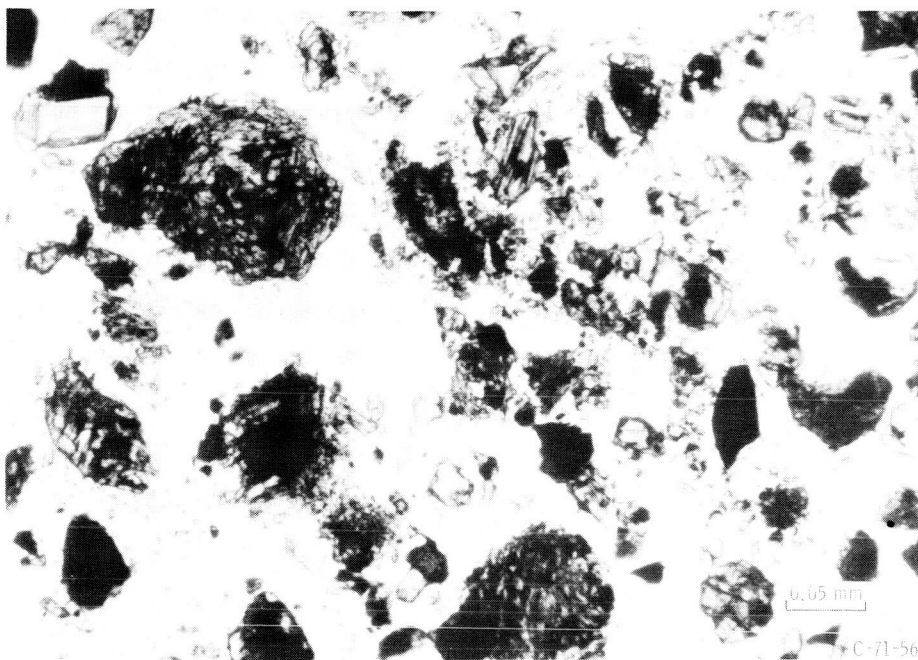


Figure 2. - Time - pressure profile at 53.3 kN/m² (400 torr) fluorine.



(a) Polarized transmitted light.



(b) Transmitted light.

Figure 4. - Reacted lunar soils (simulated).

powder with specific lack of any color. The colored phase formed after reaction with fluorine was also observable with the naked eye. The small highly fractured grains of pyroxene provide a large surface area, which may be the principal reactant site.

Photographs of the samples were taken on the unreacted material (fig. 3) and after exposure to fluorine (fig. 4).

Analysis of the residual gas from the 523 K (250° C), 53.3 kilonewton per square meter (400 torr) run was performed by reacting the fluorine in the gas mixture with mercury followed by a mass spectrometer analysis, which showed SiF₄ and oxygen to be present. This agrees with weight loss data if the weight loss is assumed to be due to the formation of volatile SiF₄ according to equation (1). The oxygen found in the gas sample represents about 4 percent of the maximum theoretical amount of oxygen available in all the components of the lunar fines.

CONCLUDING REMARKS

From the data obtained it appears that, under the temperature and pressure conditions considered here, the liberation of oxygen is inefficient. The efficiency might be improved by going to more stringent conditions, by continuous separation and recycling, or by specific selection of pyroxene-rich lunar material.

Lewis Research Center,
National Aeronautics and Space Administration,
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